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* Assisted by the Joint Program of the AEC and the ONR.

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The Dependence of a Nuclear Magnetic Resonance Frequency upon Chemical Compound*

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IN the course of measurements on N^{14} , mentioned in the previous letter, we made the surprising observation that its frequency of resonance, in liquid samples, depended strongly upon the chemical compound in which it was contained.^{1,2} This effect is strikingly demonstrated by the appearance of two resonances, separated by 1.6 kc in the neighborhood of 3300 kc, corresponding to a field of 10,500 gauss, using a solution of NH_4NO_3 in 2.0-molar $MnSO_4$ as a sample. These resonances presumably arise from the NH_4^+ and NO_3^- complexes, since samples of $NH_4C_2H_3O_2$ and HNO_3 separately give rise to two different resonances whose frequencies approximate those from the above sample. The separation is four times greater than the line widths measured between points of maximum slope.

We have observed, within a resolution of 0.1 kc, that the N^{14} resonances from the ion NH_4^+ from the compounds NH_4NO_3 , $NH_4C_2H_3O_2$, and MH_4Cl coincide at one frequency, while those from the ion NO_3^- from the compounds NH_4NO_3 , HNO_3 , and $Cu(NO_3)_2$ coincide at another frequency. Measuring the N^{14} resonances from other molecules relative to that arising from the ion NO_3^- from HNO_3 or NH_4NO_3 , we have obtained the results given in Table I. All such frequency shifts have been in the direction of lower frequency.

The separations of resonances from four pairs of compounds were also measured at 6700 gauss, corresponding to a frequency of 2100 kc, to determine whether or not the frequency separations were independent of the field intensity. They are apparently proportional to it, for the ratios of the separations are in agreement

TABLE I. Frequency shifts relative to the resonance from the ion NO_3^- at 10,500 gauss.

Compound observed	Frequency shift (kc)
NH_4^+ from NH_4NO_3 , $NH_4C_2H_3O_2$, NH_4Cl	-1.0
Liquid NH_3 , containing 0.6-molar $Cr(NO_3)_3$; NH_4OH	-1.2
$(NH_2)_2CO$	-1.0
KCN	-0.2

TABLE II. Resonance frequency separations with different compounds and field intensities.

Compounds compared	Separation (kc) at		Ratio
	10,500 gauss	6700 gauss	
NH_4^+ and NO_3^- from 7.5-molar NH_4NO_3 in 2.0-molar $MnSO_4$	1.6	0.9	0.58
HNO_3 and $NH_4C_2H_3O_2$	1.0	0.7	0.70
HNO_3 and $(NH_2)_2CO$	1.0	0.6	0.60
NH_3 , containing 0.6-molar $Cr(NO_3)_3$ and NO_3^- , from NH_4NO_3	1.2	0.7	0.58

with the ratio $6700/10,500=0.64$, within our experimental resolution. (See Table II.)

We further made the observation that the separation of the two resonances arising from NH_4NO_3 was dependent on the concentration of the paramagnetic salt $MnCl_2$ added to it. A 7.5-molar solution of this salt without $MnCl_2$ shows two resonances separated by 1.0 kc, as given in Table I, but with 1.0- and 2.0-molar concentrations of $MnCl_2$ the separations become 1.4 kc and 1.6 kc, respectively.

We shall continue to investigate this phenomenon because of its direct significance for the interpretation of nuclear magnetic resonance frequencies in terms of nuclear moments, as well as to obtain an insight into its origin. With the largest observed line shift amounting to about 5 parts in 10^4 , this effect is almost twice as large as the total diamagnetic correction calculated for the atom. These calculations, however, do not hold for the polyatomic molecules which we have studied and appreciable modification of the diamagnetism, as well as terms due to induced paramagnetism (high frequency matrix elements) can be expected, particularly in cases where three out of seven electrons may be strongly influenced by the chemical bond. The fact that the shifts are of the same order of magnitude as the diamagnetic correction and exhibit likewise proportionality to the applied field suggests a similar origin, although we have not been able to explain satisfactorily the observed magnitude of the effect. Until it is clearly understood, the accuracy of magnetic moments determined under certain chemical conditions remains somewhat in doubt.

We should like to express our appreciation to Professor Felix Bloch for stimulating discussions about this work.

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¹W. C. Dickinson, at M. I. T., has also observed similar shifts for F^{19} in different compounds. We are grateful to Professor F. Bitter for communicating this information to us.

²W. D. Knight, *Phys. Rev.* **76**, 1259 (1949), has observed a large frequency difference between the nuclear magnetic resonance frequency of a metal and its salt. The satisfactory explanation which he has given for this difference does not apply, however, to our case.

Spallation Products of Arsenic with 190-Mev Deuterons*

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RECENT investigations¹ of the nuclei formed when arsenic is bombarded with 190-Mev deuterons in the 184-in. cyclotron have been extended.

The target material consisted of twice sublimed arsenic. Spectrographic analysis² showed no impurity in sufficient quantity to account for the formation of any of the isotopes reported here with the observed yield.

The use of improved chemical separations and counting techniques has enabled the identification of 38 nuclear species among the elements from chromium through selenium. Table I lists the isotopes identified, the observed and the "nominal" half-lives as reported in the literature,³ and the yields relative to that of As^{72} taken as 1.00.

In calculating yields, the extent of electron capture has been taken from the data collected in reference 3. For Se^{73} , Ge^{69} , and Ga^{66} , crude absorption measurements indicated that approximately two-thirds of the decays are by electron capture. The yield of As^{72} is based on the count of beta-particles, as no x-rays were observed (< 50 percent of the disintegrations). The yields reported here should all be accurate to within a factor of two and many accurate to within 20 percent, depending on the certainty with which electron-capturing ratios and counting efficiencies of x-rays are known.

Table I contains two changes in isotope assignment differing from those previously reported.¹ The 44-min. selenium and 52-min.